R94-958345-F

NONLINEAR OPTICAL DIAGNOSTICS OF NITRAMINE COMBUSTION

Final Report

J. H. Stufflebeam

April, 1994

Office of Naval Research
Contract: N00014-90-C-0121

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East Hartford, Connecticut 06108

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NONLINEAR OPTICAL DIAGNOSTICS OF NITRAMINE COMBUSTION

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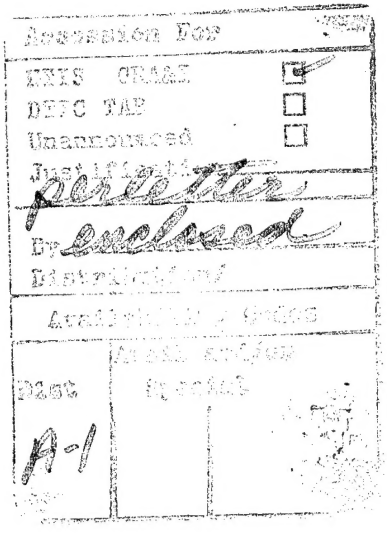
Executive Summary

The specific technical achievements of this Office of Naval Research contract are as follows. The use of a high pressure, motorized combustion vessel allowed control of the spatial location of the burning propellant surface and data acquisition from the thin (100 micron), near-surface reaction zone. Resolution of the temperature and species profiles in the reaction zone, required for further insight, was provided by a major advance, the implementation of Line CARS, a 1-D imaging geometry, that allows single shot (10 nsec) measurement of the large temperature and concentration gradients near the surface with a spatial resolution of 25 microns. Partial funding of the Line CARS work was provided under ARO Contract DAAL03-87-C-0005. An internal heater was designed and implemented in the motorized vessel that allowed the preheated strand to sustain combustion at low pressure (1 atm) with expanded reaction zones and increased spatial resolution. CARS was used to study the concentration profile of NO immediately above the surface of a nitramine flame at 2 atm pressure. Degenerate four wave mixing (DFWM) was investigated for diagnostics of minor combustion species in propellant flames. Laboratory flames were first used to investigate the DFWM signal of OH at pressures from 1 to 5 atm and compare the spectra to that from LIF. A significant achievement of this contract is the first DFWM spectrum of CN observed in a flame. A difficulty was encountered late in the program; satisfactory combustion diagnostics of ADN was not accomplished in the strand burner. Excessive AN smoke and fuel particles caused laser breakdown and precluded the acquisition of data from ADN combustion.



Introduction

There have been significant recent advances toward understanding solid propellant combustion. Propellants and explosives based on nitramines provide many of the modern propulsion fuels and ballistic systems. Optical diagnostics have contributed greatly to our knowledge of solid propellant combustion chemistry, primarily in studies conducted in surrogate flames. Laser diagnostics are remote, nonintrusive and generally have high spatial and temporal resolution. Measurement capabilities include temperature, and concentration of both major and minor combustion species. The optical techniques utilized for combustion investigations include emission, absorption, fluorescence, and nonlinear optical diagnostics, *e.g.,* CARS and DFWM. Emission and absorption are line of sight measurements and have poor spatial resolution; fluorescence measurements suffer from uncertainties of quenching corrections, and the technique becomes very difficult to apply in high pressure combustion. Nonlinear techniques do not suffer quenching effects and have been demonstrated over a wide pressure range. Particularly, CARS has produced very good results in nitramine combustion at elevated pressure. The nonlinear techniques derive from the medium response to stimulation by radiation through the third order nonlinear susceptibility. CARS relies on enhanced sensitivity at Raman resonances of the medium. Other nonlinear optical techniques rely on stimulating other resonances of the medium; for degenerate four-wave mixing (DFWM), the targeted resonances are electronic transitions of the molecules. The minor species in combustion, particularly radical species have electronic transitions in the uv that can be utilized for diagnostic measurements. Particular molecules of interest for energetic materials combustion pertain to nitrogen chemistry and include CH, CN, OH, NH, and NO. All these have transitions in the uv that could be probed with DFWM. In general, measurements of these minor, radical species complement the CARS measurements of major combustion species and temperature. The goal of this research program is to use one of the most successful laser diagnostics, CARS, together with the development of DFWM, to probe energetic material combustion. The program investigated the combustion chemistry of polycyclic nitramines through temperature and multiple-species measurements that extend the capability of the diagnostic techniques and knowledge of the combustion chemistry.

Research Goals

The specific research goals of this contract were:

CARS measurements. Acquire CARS temperature and species data from nitramines to compare with the combustion models. The data will be acquired over the pressure range 1-20 atm of nitramine combustion. This goal is documented in the invited paper "CARS Temperature and Species Measurements in Propellant Flames," by John H. Stufflebeam and Alan C. Eckbreth, presented at the 3rd International Symposium on Special Topics in Chemical Propulsion: Non-Intrusive Combustion Diagnostics, held in Scheveneningen, The Netherlands, May, 1993. This paper is included in Appendix B.

DFWM investigations. Investigate DFWM in atmospheric pressure flames relevant to the Navy program in solid propellant combustion, *i.e.*, CH_4/O_2. Attention was focused on OH and CN because of the interest to nitramine chemistry. Experiments in flames of increasing pressure is required to check linewidth effects that may impact the accuracy of measurements. Our initial experiments with DFWM of OH at low pressure are included in the paper in Appendix B. Concurrent with this contract although not directly funded by it, a significant advance in the DFWM technique was invented at our laboratory. Double phase conjugate four wave mixing (Winter and Radii, 1992) allows maintenance of laser focal alignment through the strong refractive index gradients of flames (especially at high pressure) that would otherwise restrict accurate measurements in these hostile environments. Results from experiments utilizing this technique are also presented in the paper in Appendix B. Our more recent experiments in DFWM, including spectra from OH up to 5 atm and CN in an acetylene/nitrous oxide flame are fully described later in this report.

Comparison of DFWM and LIF. LIF spectra were obtained simultaneously with the DFWM data and differences in spectral quality were assessed. This is detailed for OH in Appendix B.

Broadband approaches to DFWM. Another consideration for the high pressure, turbulent environment of propellant combustion is the need to make multiple species and temperature measurements rapidly as has been demonstrated in our CARS experiments. DFWM techniques need to be developed that allow this rapid measurement as well; these techniques probably require broadband DFWM to interrogate more than one molecule or transition simultaneously. This phase of development will include optimum strategies to produce the broadband source, *i.e.*, double a broadband source or utilize a broadband excimer laser or dye laser that is pumped by an excimer or harmonic of Nd:YAG. Alternately, a multiple-beam source may be developed by combining several narrowband sources.

DFWM measurements of nitramine combustion. Apply DFWM to 'neat', polycyclic nitramine combustion. Satisfactory combustion of ADN was not accomplished in the strand burner. Excessive AN smoke and fuel particles caused laser breakdown and precluded the acquisition of CARS or DFWM data from ADN combustion. More details of this phase of the work is included in the next section.

Technical Accomplishments

Many of the technical accomplishments of this contract are presented in the invited paper "CARS Temperature and Species Measurements in Propellant Flames," by John H. Stufflebeam and Alan C. Eckbreth, presented at the 3rd International Symposium on Special Topics in Chemical Propulsion: Non-Intrusive Combustion Diagnostics, held in Scheveneningen, The Netherlands, May, 1993. This paper is included in Appendix B. Specific work discussed in this paper and funded under this contract includes Line CARS (also partially funded by the Army Research Office through Contract DAAL03-87-C-0005) to measure the temperature and species

gradients immediately above the surface during propellant combustion. Also during this contract and described in the paper, the motorized combustion vessel was upgraded with an internal heater used to preheat samples to a uniform temperature which allows combustion below the deflagration pressure. The results of 1 atm combustion are presented in Appendix B. Experiments that were not presented or are more recent than those in the paper are discussed in the following paragraphs.

Near-surface gradients of low pressure combustion in XM39, NO data. Line CARS was utilized for high spatial resolution at 20 atm combustion but is not useful at low pressure because of the density-squared scaling of the CARS signal, the signal would be too small to recover without multi-pulse averaging and this technique is not advocated for turbulent combustion environments. Solid propellant combustion at low pressure, conducted at other laboratories and extensively studied by scientists investigating fundamental combustion chemistry, expands the near surface reaction zone to several millimeters for which normal, single point CARS with 115 micron resolution is adequate. These experiments provide data compatible with other programs in fundamental combustion of energetic materials.

The following figures demonstrate the acquisition of CARS spectra from nitramine propellants at low pressure. Figure 1 is a dual broadband CARS spectrum acquired 5 mm above the surface of XM39, an RDX based propellant, at 2 atm. The dual broadband technique (Eckbreth and Anderson, 1986) provides a broader bandwidth sensitivity to acquire more signatures with each CARS spectrum. The signatures of H_2, NO, HCN, CO and, N_2 are evident in Fig. 1. This data is an average of several laser shots at a constant position above the surface.

It is important to investigate the spatial profile of these molecules above the surface. Results from these experiments are shown in Fig. 2. In this experiment, XM39 was burned at 2 atm but the servo system did not control the strand position; the strand was allowed to burn down past the laser focus and spectra were acquired at the 10 Hz pulse rate of the laser. These spectra are averaged for 2 seconds (20 pulses) to improve the signal to noise. During this time the strand moves 800 microns, but the spatial distribution of species concentration and temperature is still resolved at this low pressure. Similar results were obtained with 1 second averaging (400 micron spatial resolution) with slightly lower S/N. In Fig. 2, the spatial distribution of the NO, HCN and H_2 are clearly resolved. The H_2, an equilibrium product, does not show up until the intermediate NO and HCN have started to decrease in amplitude.

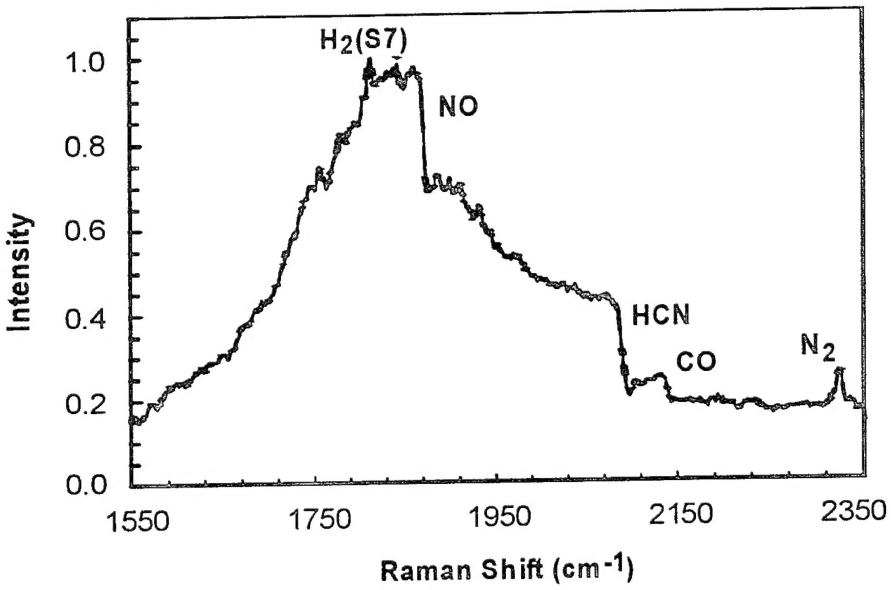


Figure 1. Dual Broadband CARS spectrum from XM39 combustion at 2 atm. Spectrum was acquired 5 mm above propellant surface.

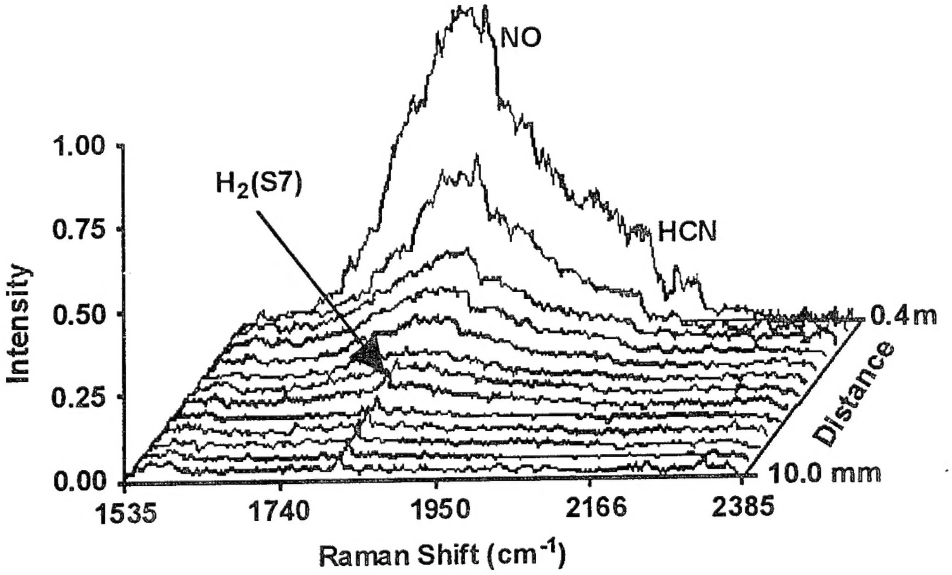


Figure 2. Dual broadband CARS spectra showing spatial distribution of NO, HCN and H_2 immediately above the surface of XM39 burning at 2 atm.

ADN Combustion. Research samples of ADN crystals were received from Chemical Systems Division of United Technologies. Precautions were followed for storing this oxidizer; no exposure to uv light or high humidity.

The ADN powder was measured into 10-2.5 gram samples under a nitrogen atmosphere in a glove bag. The samples were transferred to a Perkin-Elmer die and pressed to 8000 lbs by a 0.509" plunger (40,000 psi). During the pressing procedure, a vacuum was maintained on the sample and the only lighting used in the room was a portable incandescent bulb. A desiccant (calcium sulfate) was present in the glove bag to reduce humidity. After pressing the samples, the pellets were pressed out of the die and stored in a black, static resistant, plastic bag with the desiccant container.

Combustion experiments were initiated at 5 atm of air background pressure at a high flow rate, 80-100 l/min. The ADN did not require preheating, ignition was easily accomplished even at 1 atm. The smoke produced by pure ADN combustion inhibited laser diagnostics with the high power Nd:YAG laser. Consultation with personnel at China Lake resulted in plans to mix some fuel with the oxidizer to reduce the AN smoke. Beeswax (yellow, refined) was acquired from Aldrich Chemical company. The wax is supplied in large chunks, unsuitable for mixing with the ADN. The first attempt to reduce the size of the fuel particles utilized a cheese grater but this was unsuccessful because of clogging in the grater pores. A successful approach required freezing the beeswax in liquid nitrogen then crushing it with a mortar and pestle. The crushed beeswax was then screened to retain only the small particles (~100 micron dia.). There was concern that when the beeswax warmed up it would coagulate but this was not the case, it remained small particles and required no special storage requirements. The ADN and beeswax were measured out under a nitrogen atmosphere inside a glove bag that also contained a desiccant chemical to reduce the ambient humidity. The chemicals were mixed and pressed into pellets the same size as the pure ADN samples. The mixture was 2.0 grams of ADN and 0.5 grams of beeswax in each 13 mm dia. pellet. The mixture was pressed to 25,000 psi in the Carver press. Safety concerns limited the ultimate pressure, the mixture is probably more sensitive to friction and handling than the pure ADN because the mixture is closer to a combustion stoichiometry. A stainless steel plate structure was assembled and deployed around the press for protection of the personnel in case of ignition and explosion during the processing. Plastic gloves were also used for all contact with the chemicals, both for protection of the people involved and to avoid contamination of the chemicals. There were no complications during the processing. The pellets were stored in a black polyethylene bag specially treated to reduce static charge build-up. A container of desiccant was also included in the bag with the pellets to reduce the local humidity during storage in the propellant safe. Unfortunately, this mixture still produced copious smoke and also fuel particles in the combustion products which caused laser breakdown. Reduction of laser intensity to avoid the problem resulted in inadequate power to produce a broadband CARS signal above the noise of the detector.

DFWM data of OH at elevated pressure. Figure 3 is a DFWM spectrum of the R, P, and Q branches of the $A^2\Pi(v'\text{-}0)\text{-}X^2\Sigma^+(v''\text{-}0)$ transition of OH. It was obtained in a 5 atm methane/air premixed flame. This spectrum was obtained with the experimental apparatus described in Appendix B; it represents normal DFWM, not the double phase-conjugate geometry. The narrowband dye laser was implemented by frequency doubling a solution of Rh610 in methanol pumped with the 2nd harmonic of Nd:YAG. This Doppler free spectrum has very good S/N and narrower linewidths than the LIF spectrum at this pressure (Bervas et al., 1992; Feikema et al., 1992).

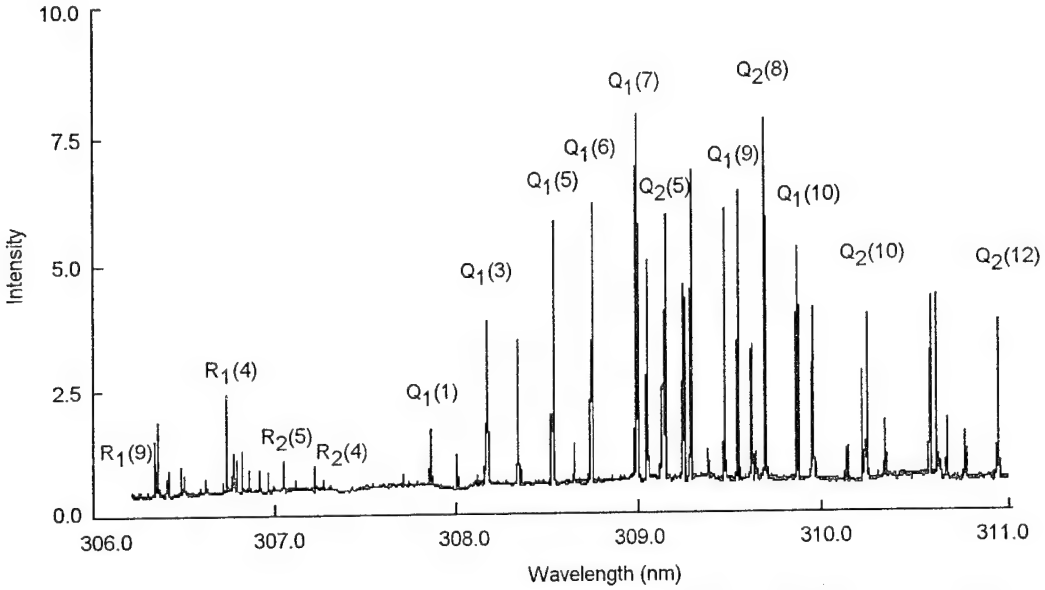


Figure 3. DFWM spectrum of OH from a premixed methane/air flame at 5 atm.

Double phase conjugate, four wave mixing of CN. The experimental geometry is shown in Fig. 4. The uv wavelengths required of the absorption transitions are provided in a Lumonics 500D dye laser that is pumped by the 3rd harmonic of Nd:YAG. The CN transitions were accessed by pumping the dye LD390 to produce narrowband (0.001 nm) pump and probe beams at the 388 nm wavelength. The first beamsplitter separates 50% of the uv laser to produce a probe beam that is directed through the flame. The forward pump crosses the probe, within the flame, and subsequently is phase conjugated in the Brillouin cell and propagates backward identically along itself to form the backward wave. Any phase aberrations that distort the forward pump are reversed during the traversal of the backward pump, maintaining alignment and optimum phase matching. The signal beam propagates backward along the probe direction and is separated from the probe at the 50% beamsplitter. It is then detected on the photomultiplier, sampled by a gated integrator, and digitized and stored in a computer. Similarly, the LIF is detected at 90° from the direction of the pump beams. Scanning the frequency of the dye laser produces the DFWM and LIF spectrum.

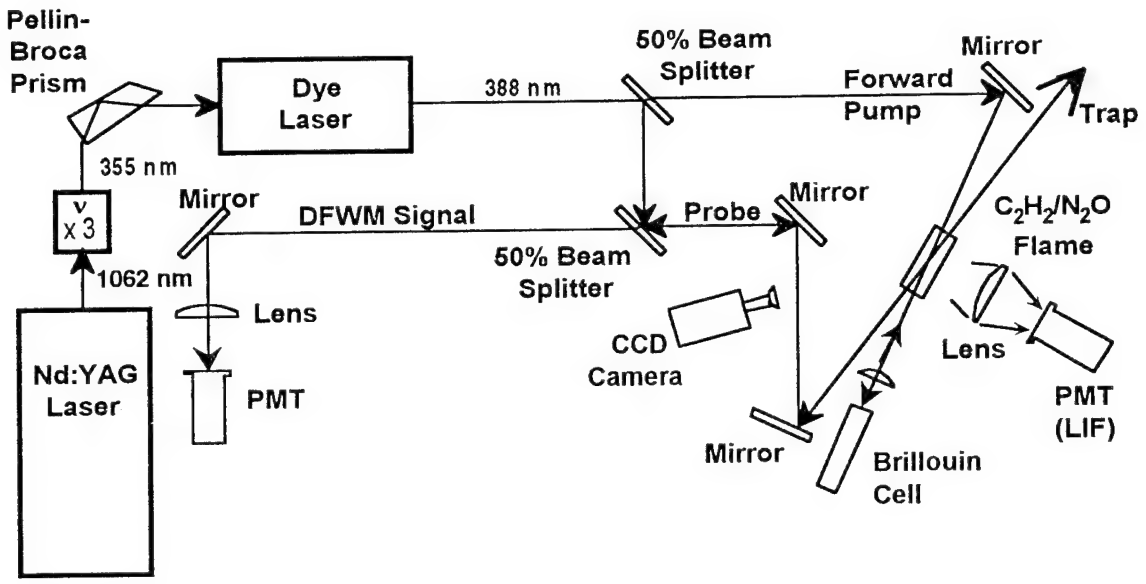


Figure 4. Optical layout for double phase-conjugate four wave mixing. Laser wavelength is at the CN(0,0) absorption band.

Shown in Fig. 5 is the DFWM spectrum of CN in an atmospheric pressure, premixed, C_2H_2/N_2O flame. These data were obtained by scanning the narrowband laser through the absorption transitions of CN. The portion of the spectrum containing the P and R branch of the $B\,^2\Sigma^+(v'=0)$-$X\,^2\Sigma^+(v''=0)$ transition is shown. The spatial resolution was determined by the intersection of the pump and probe beams and was approximately 1 mm^3.

Temperature Analysis. Abrams (1983) provided a theoretical basis of DFWM; his analysis of equal intensity pump beams that strongly saturate the transition in weakly absorbing media predicts a signal intensity of:

$$I_S = \frac{a_0^2 L^2 I_p}{16\,(I/I_{sat})}$$

where a_0 is the absorption coefficient, L the interaction length and, I_p the pump intensity. Experiments that employ double phase-conjugate geometry are generally strongly saturated because of the threshold intensity necessary to achieve moderate reflection in the stimulated Brillouin cell.

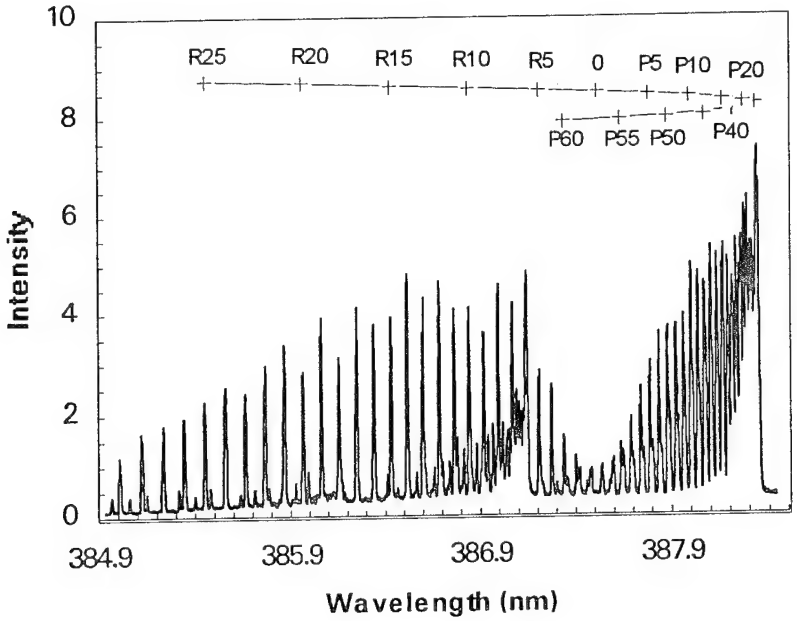


Figure 5. DFWM spectrum of the CN(0,0) violet band. C_2H_2/N_2O flame at 1 atm. Resolution is 0.02 nm.

Dreier and Rakestraw (1989, 1990) and Farrow and Rakestraw (1992) have shown that DFWM line intensities of OH, NO and NH transitions in atmospheric flames scale simply with the square of the rotational state number density. Williams (1992) showed the same scaling for CH.

$$I_S \propto B_{ij}^2 (\Delta N)^2$$

where ΔN_2 is the population difference between the levels of the transition and the line strength is

$$B_{ij} = \frac{f_{v'v''} S_{N'N''}}{(2N''+1)}$$

Colket (1984) measured the oscillator strength of CN transitions, $f_{v',v}$, and the Hönl-London factors for the R-branch transitions are

$$S^{R}_{N'N''} = \frac{(N''+1)^2 - 1/4}{N''+1}$$

If an equilibrium thermal distribution is assumed for the rotational populations, they are represented by the Boltzmann factor,

$$\Delta N \propto e^{\frac{-B_{v''}N''(N''+1)hc}{kT}}$$

Then a plot of $\mathrm{Ln}(\sqrt{I_s}/B_{ij})$ vs $N''(N''+1)$ will yield a straight line with a slope of $-B_{v''}hc/kT$. The least squares fit to the data includes only the higher rotational levels (N">15) of the R branch, they are less congested by the overlap with transitions of the returning P branch and rotational transitions of the higher vibrational states (v'=1, v"=1 and v'=2, v"=2). The regression fit (Fig. 6) predicts a rotational temperature of 3150K. Bonczyk and Shirley (1979) measured a rotational temperature of 2900K from absorption data in this same flame facility.

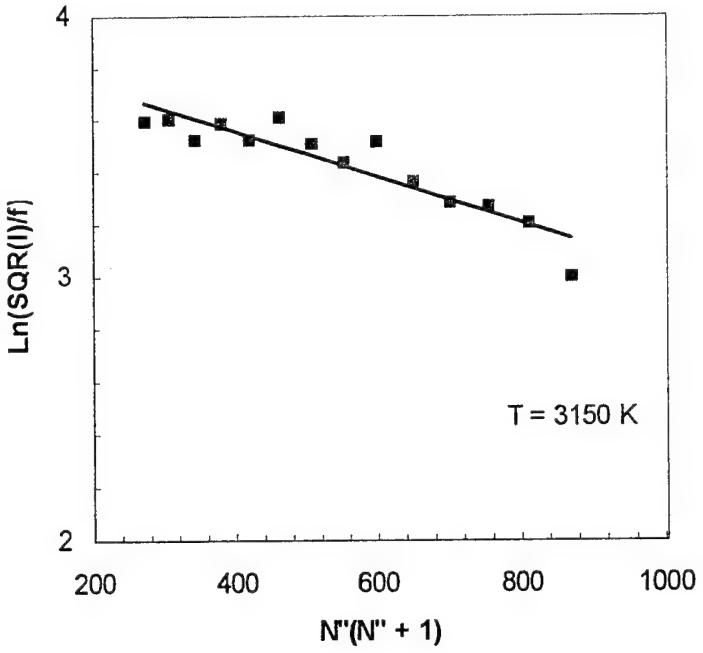


Figure 6. Boltzmann plot of rotational population distribution in the R branch of CN(0,0). N"=15 to 29 are included.

Comparison of DFWM and LIF. DFWM and LIF spectra of OH at 1 and 2 atm were discussed in the paper in Appendix B and references therein. Whereas LIF intensities are linearly proportional to the state population but have additional, complicated quenching corrections that must be applied for concentration measurements. The Doppler free DFWM spectrum has narrower linewidths than the LIF spectrum, thus higher resolution and comparable sensitivity to the LIF spectrum. The quenching corrections increase the relative error associated with LIF measurements. Quantitative DFWM measurements would complement CARS data of temperature and the major combustion species and provide more of an experimental database to compare with predictions from combustion models. Recent experiments have focussed on CN and the goal of understanding N_2 chemistry. High resolution DFWM spectra are presented and discussed in the next section.

Broadband DFWM. The investigation of broadband DFWM targeted the CN molecule. It is necessary to acquire enough spectral information in each 10 nsec laser pulse to estimate the concentration and temperature. Propellant burn times, measured in seconds in the strand burner, are not long enough to acquire a high resolution spectrum like Fig. 5. Adequate information is contained in a few (<10) transitions if they have a large variation in intensity and thus a high sensitivity to temperature. The bandhead of CN is such a region and higher resolution scans of the bandhead region were acquired with a resolution of 0.0005 nm. These data are shown in Figs. 7. The region is very congested with overlaps of the P branch transitions; they are barely resolved in these figures. A low resolution DFWM spectrum could encompass several of the transitions and its shape would be very sensitive to temperature. The Lumonics laser can be operated in a broadband mode that would cover a region of 1 or 2 nm, sufficient to include more than 50 transitions. It is difficult to accurately estimate the width of broadband DFWM spectra because they will depend inherently on the phase matching geometry and properties of the nonlinear medium. This question is best left to experimentation. The broadband spectra need to be acquired from several different flame stoichiometries (different flame temperatures) and can be calibrated from simultaneous absorption spectra. Theoretical models are also required of the temperature sensitivity of the low resolution spectra so that temperatures can be predicted fromexperimental data.

Conclusions

The implementation of Line CARS, a 1-D imaging geometry, allows single shot (10 nsec) measurement of the large temperature and concentration gradients near the surface with a spatial resolution of 25 microns. An internal heater in the motorized vessel allowed the preheated strand to sustain combustion at low pressure (1 atm) with expanded reaction zones and increased spatial resolution. CARS spectra containing the concentration profile of NO immediately above the surface of a nitramine flame at 2 atm pressure were obtained. Degenerate four wave mixing (DFWM) was shown to be sensitive to radical species of interest in propellant

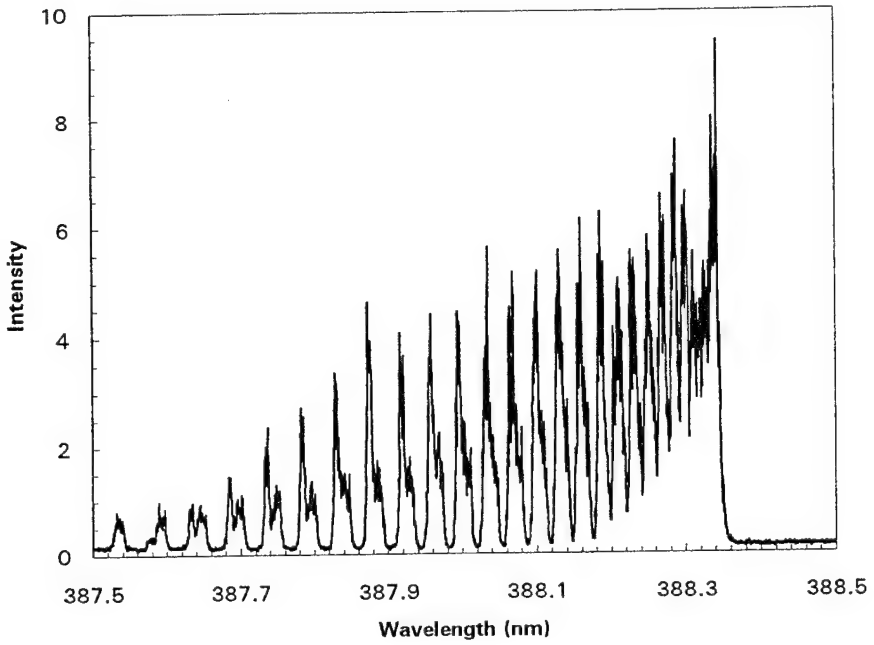


Figure 7. DFWM spectrum of the CN(0,0) violet band. C_2H_2/N_2O flame at 1 atm. Resolution is 0.0005 nm.

combustion. The DFWM signal of OH in laboratory flames, at pressures from 1 to 5 atm, was acquired and compared to the spectra from LIF. A significant achievement was the first DFWM spectrum of CN observed in a flame. The DFWM data was analyzed to predict the flame temperature of 3150K. Satisfactory combustion diagnostics of ADN were not accomplished in the strand burner. Excessive AN smoke and fuel particles caused laser breakdown and precluded the acquisition of data from ADN combustion.

Recommendations for Future Work

The development of the broadband approach to DFWM for single shot concentration and temperature measurements should be continued. The double phase conjugate approach has advantages for maintaining laser beam alignment in turbulent combustion environments and should be pursued. Degenerate four wave mixing also is amenable to 2-D imaging of molecular species and this is very important data for combustion modelers. The imaging experiments could be conducted in the flame environments suggested for the broadband studies and should be investigated for the potential data of propellant flame structure.

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APPENDIX A

Publications/Presentations Under ONR Contract N00014-90-C-0121

Stufflebeam, J. H., "Near Surface CARS and DFWM of Propellant Flames", invited paper presented at the 1990 Gordon Conference on the Chemistry of Energetic Materials, New Hampton School, New Hampton, NH, June 25-29, 1990.

Stufflebeam, J. H., "CARS Measurements in the Near Surface Region of Composite Nitramine Combustion", presented at the 27th JANNAF Combustion Meeting, Warren AFB, Cheyenne, Wyoming, November 5--9, 1990. CPIA Publication 557, Vol. 3, pp. 57-65.

Stufflebeam, J. H., "CARS Diagnostics of Reaction Pathways for Nitramine Combustion", presented at the AIAA/SAE/ASME/ASEE 27th Joint Propulsion Conference, Sacramento, California, June 24-27, 1991.

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APPENDIX B

CARS Temperature and Species Measurements in Propellant Flames

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Presented at

Third International Symposium on
Special Topics in Chemical Propulsion:
Non-Intrusive Combustion Diagnostics
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CARS Temperature and Species Measurements in Propellant Flames[1]

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ABSTRACT

Measurements of species, temperature, and their gradients are necessary for accurate modeling of solid propellant reaction mechanisms and their effect on the combustion characteristics of the propellant. The very difficult experimental problems posed by solid propellant combustion environments challenge even the most modern diagnostic techniques. CARS (coherent anti-Stokes Raman scattering) and DFWM (degenerate four-wave mixing) are coherent nonlinear, laser-based, optical diagnostics with high spatial and temporal resolution that accommodate well to the high interference and restricted optical access environments typical of solid propellant combustion experiments. CARS measurements at our laboratory have confirmed the equilibrium chemistry (temperature and species concentration) of nitramine propellant formulations burning at elevated pressures. A 1-D imaging configuration, realized with cylindrical optics and a 2-D detector, provides enhanced spatial resolution and single-shot data on species and temperature gradients adjacent to the strand surface during high pressure combustion. An experimental program, currently underway to obtain CARS and DFWM measurements near the surface of combusting energetic materials at atmospheric pressure using a motorized strand burner, will also be described.

INTRODUCTION

Understanding the transient, turbulent nature of solid propellant combustion requires measurement technology which has high temporal and spatial resolution, and which can handle the severe combustion conditions of high luminosity and high particle loading. Detailed, spatially and temporally precise, measurements of temperature and species concentrations of the products of the intermediate chemical reactions are most important in nitramine combustion experiments. Such results seek to identify dominant reaction mechanisms that can be affected by parameters such as fluid dynamics, transport properties, or autocatalysis. In particular, information is desired of the regions close to the propellant surface, i.e., the fizz zone or primary reaction zone, which require a very high spatial resolution technique. Diagnostics that couple temperature with species concentration measurements are preferred.

It is evident from the literature (Adams and Shaw, 1992; Fifer, 1984) that nitrogen chain chemistry is one of the most important to study for the purposes of understanding propellant

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behavior. Fundamental pyrolysis, calorimetry and thermogravimetric experiments (Behrens and Bulusu, 1991, 1992) have demonstrated that nitramines decompose to form NO_2 as a major oxidizer with HCN, and possibly H_2CO, as probable fuels. The discussion of nitramine chemistry (Melius, 1988) shows that the important molecules to measure in the gas phase are HCN, NO, N_2O and H_2CO.

Optical diagnostics offer an opportunity for propellant combustion measurements. They are remote and non-intrusive and can be designed for high spatial and temporal resolution. Laser based combustion measurements are approached through consideration of the target measurements, i.e., major or minor species. Raman-based techniques can be used for major species while minor constituents require electronic resonance based diagnostics. Further choices involve either coherent or incoherent implementations of each approach, resolved through consideration of optical access and interferences which can degrade the signal.

Incoherent approaches, such as spontaneous Raman scattering or laser-induced fluorescence spectroscopy (LIFS), scatter their signal into 4π steradians and require large optical apertures to collect adequate signal. The large aperture presents the opportunity for unwanted interferences, e.g., laser scatter or emissions, to be collected with the desired signal. Spontaneous Raman scattering, used for major species diagnostics, affords the advantage of spectral separation of the signal from the pump laser frequency, easing rejection of unwanted laser scatter and enhancing the signal-to-noise ratio. It is a weak process, however, and often requires averaging for many laser pulses to acquire adequate signal to noise. LIFS is the incoherent diagnostic of choice for minor combustion species. It is a linear process achieved by tuning into electronic resonances and monitoring the spontaneous emission. The signal is generally strong, although detailed information of the interrogated medium is required to properly interpret quenching effects and analyze the data.

Coherent optical diagnostics are more difficult to apply, but the coherence allows collection of the total signal within a narrow aperture. This is an advantage for high pressure combustion experiments where optical access is often restricted to small ports. Of the coherent techniques, coherent anti-Stokes Raman spectroscopy (CARS) has matured over recent years and is used extensively in combustion research experiments. It is utilized for temperature and major combustion species measurements. Degenerate four-wave mixing (DFWM) is the complementary, electronic resonance, coherent technique that is sensitive to minor combustion species. It has only recently been employed as a diagnostic in combustion experiments and is not as mature as the other techniques mentioned, but may have advantages for hostile, high pressure environments such as propellant combustion.

These coherent techniques have been used and are being adapted to propellant combustion measurements in our laboratory. A comprehensive review of CARS is given in Eckbreth (1988), and this diagnostic has been successfully applied to nitramine combustion by Stufflebeam and Eckbreth (1989). CARS measurements of temperature and major combustion species are described in the next sections of this paper. DFWM is also being studied in our laboratory and, although fewer measurements have been obtained, results are encouraging for minor species measurements near the propellant surface where the usual molecules used for CARS thermometry may be absent, precluding temperature measurements in this very important region. These experiments are discussed in the latter sections of the paper.

COHERENT ANTI-STOKES RAMAN SPECTROSCOPY

Nonlinear optical techniques depend on the medium's nonlinear response to radiation, characterized by the third-order polarization of the medium.

$$P^{(3)}(\omega_4) = \chi^{(3)} E(\omega_1) E(\omega_2) E(\omega_3)$$

The optical fields are represented by their amplitudes, $E(\omega_i)$, where ω_i is the frequency of the wave. The third-order nonlinear susceptibility, $\chi^{(3)}$, contains the characteristics of the medium that are important for analysis of the signal, i.e., quantum state populations, resonances, transition linewidths, etc. For CARS, these resonances are Raman rovibrational transitions. The frequencies of the pump lasers are chosen to satisfy energy conservation conditions for the interactions, and result in the signal frequency being shifted from the pump frequencies according to

$$\omega_4 = \omega_{CARS} = \omega_1 + (\omega_1 - \omega_2)$$

CARS requires at least two different laser frequencies, and they are separated by the Raman transition frequency, $\omega_R = \omega_1 - \omega_2$, so that the susceptibility is vibrationally resonantly enhanced. CARS is a *non*degenerate, four-wave mixing technique. The signal is maximized if photon momentum is also conserved, i.e., $\Delta \vec{k} = 0$,

$$\vec{k}_{CARS} = \vec{k}_1 + \vec{k}_1 - \vec{k}_2$$

where, $|\vec{k}_i| = n\omega_i / c$, n is the index of refraction of the medium and c is the speed of light. Photon momentum conservation is termed "phase matching" in nonlinear optics and is achieved by mixing the fields, E_i, at the proper angles, as in the folded BOXCARS configurations of Shirley, et al. (1980). This results in a narrow, well-defined signal beam that can be easily detected, completely collected and, in addition, provides discrimination against background flame luminosity because the detection optics can be high f-number. Thus the technique is very well suited to the limited optical access ports characteristic of high pressure combustion chambers.

Temperature and concentration information is contained in the spectral intensity distribution of the CARS signal. The spectrum is composed of resonant and nonresonant susceptibility contributions. The resonant part is a function of molecular number density, temperature, pressure and various molecular parameters such as the rovibrational linewidths of the molecule. Measurements of temperature rely on determining the relative populations (i.e., Boltzmann distribution) of rovibrational states of the resonant signature. The nonresonant component is proportional to total gas density. Resonant features of molecules in moderate concentration ($\leq$ 40%) modulate the nonresonant signal, and relative concentration measurements derive from the modulation depth of the resonant signature on the nonresonant background (Eckbreth, 1988). The temperature and concentration measurements are performed by computer analysis of the acquired CARS spectra.

Experimental Hardware

The CARS approach employed here uses a frequency-doubled Nd:YAG and dye lasers operating at a 10 Hz rate with 10 nsec pulses. A folded BOXCARS configuration produces a high spatial resolution, cylindrical interaction region of $150\mu \times 3$ mm. The combustion vessel is a closed bomb modified for a background purge with inert gas. In our early work, the laser beams were initially focused 1 mm above the propellant strand (typically 12.5 mm long); the strand was ignited and regressed from the laser focus. During the regression, spectra were acquired every 100 msec which resulted in 50-60 single-shot measurements of temperature and concentration. The burns were monitored by a video camera that gave a quantitative measure of the distance between the laser focus and propellant surface for the sequential laser pulses. The propellant used for these measurements was a composite nitramine (Edwards, 1988) that contained 73% HMX, 17% TMETN and 10% polyester binder. It was burned in a background of helium which is chemically inert and has a low nonresonant susceptibility, adding negligible signal to the CARS spectra.

Spectra were acquired from pressures up to 35 atm, but most of the experiments were performed at 23 atm so that they would be compatible with LIF and emission spectroscopy work performed by Edwards (1988) on an identical propellant.

Near-surface experiments. To address the problem of measurements near the surface, the experiment was upgraded to include a motorized combustion vessel (Field, et al., 1988). It has a stepper motor to advance the propellant as it regresses, maintaining the burning surface fixed relative to the laboratory reference frame. It is capable of burning strands up to 7.5 cm long so more data can be collected during each combustion event. The motor is controlled by the servo system depicted in Fig. 1 which utilizes a laser diode and a phototransistor array to sense the burning surface location.

The diode laser is modulated at 20 KHz to discriminate against flame luminosity. The detection system demodulates the signal, and logic circuits determine the location of the surface. An error signal is generated, based upon the difference from a manually supplied reference position. The error signal is transformed through the PID (proportional, integral, derivative) electronics into a train of variable frequency pulses that drive the stepper motor through the translator. The amount of proportional, integral, or derivative feedback supplied is manually adjusted depending on experience with the device. Experiments indicate the HMX/TMETN propellant surface can be controlled to within 100μ jitter from the reference position. In any case, the distance from the laser volume to the burning surface can be measured from the video record for each individual CARS spectrum.

Line CARS. Attempts to quantify the relative importance of reaction pathways require higher spatial resolution measurements because the CARS focal diameter is 150μ and may sample the entire reaction zone at elevated pressure. A novel spatial enhancement technique was developed to apply CARS to the fizz zone of the burning propellant (Stufflebeam, 1986). To enhance the

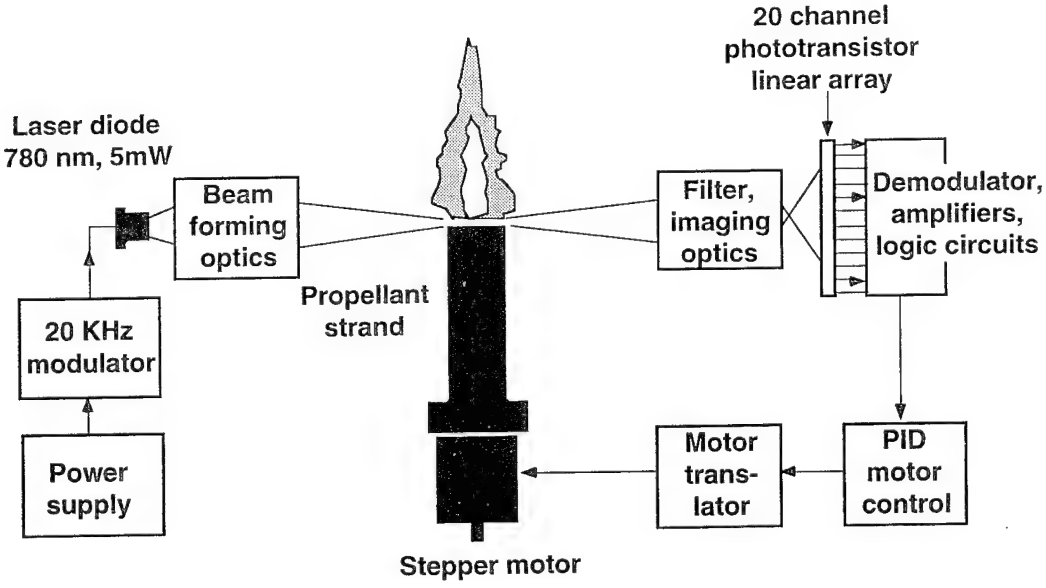


Figure 1. Laser servo system for the motorized propellant combustion vessel.

resolution and provide 1-D spectra of temperature and species concentration, a planar BOXCARS phase-matching geometry is employed with cylindrical optics to form a "line" focus perpendicular to the surface. For this technique the motorized combustion vessel is employed, with the dye laser

and the 532 nm pumps focused as sheets 0.4 mm high in a planar BOXCARS geometry immediately over the solid propellant surface, as shown in Fig. 2.

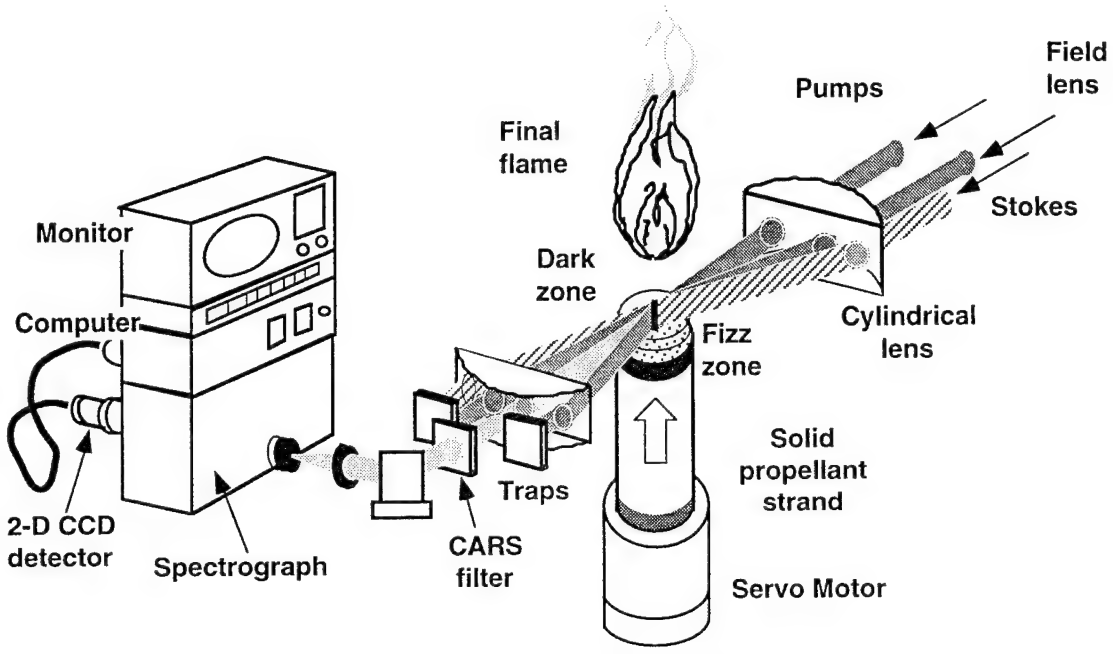


Figure 2. Linear CARS imaging geometry for gradient measurements near the propellant surface.

The surface is rough, with features (hills and valleys) approximately 10 microns in dimension, so that the fizz zone should be in the laser "line of sight." The focal zone where the CARS is generated will then be a line perpendicular to the propellant surface and extending up about 0.4 mm. Upon exiting from the burner vessel, the pump beams are blocked and the 0.4 mm CARS image is incident on the slit of the spectrograph. CCD detectors are employed for these imaging experiments; they have virtually no crosstalk, high dynamic range and very low dark current which decreases noise. The CARS spectra, when imaged on a 2-D detector, provide visualization and data for measurements of temperature and concentration profiles on a single-shot (10 nsec) basis.

1-atmosphere experiments. The combustion vessel has been upgraded with an internal heater (shown in Fig. 3) used to preheat the sample to a uniform temperature which allows combustion below the deflagration pressure. The propellant is sealed in the combustion vessel and is drawn down inside the insulated heater coils with remote controls while thermocouples monitor its temperature. This provides a very safe operating environment. A strand is heated to 80 C in about 15 minutes. When the desired uniform temperature has been reached, the propellant is raised and contacts an ignition wire. We have used this device to burn HMX at one atmosphere pressure with an extended reaction zone.

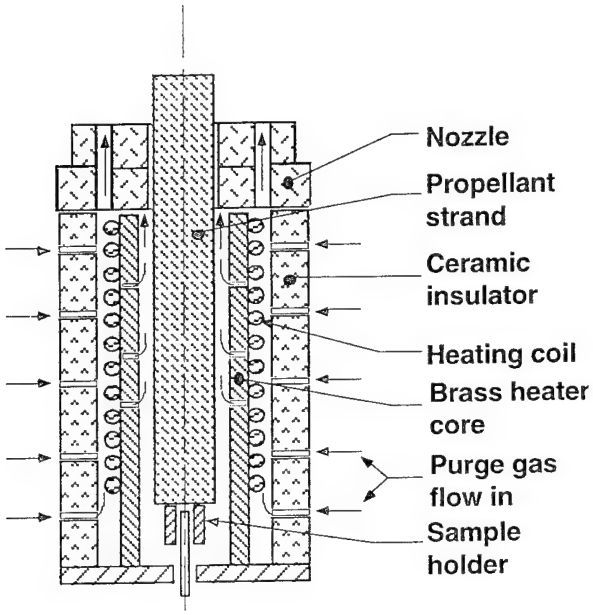


Figure 3. Internal heater assembly for the solid propellant combustion vessel.

Experimental Results and Discussion

Final flame zone. A typical single-shot CARS spectrum from a burn at 23 atm is shown in Fig. 4. The spectrum shows resonant signatures from CO, H_2, and N_2 that modulate the broader Gaussian-shaped nonresonant background signal. The gas is very hot, as evidenced by the significant population of the high vibrational states in the CO and N_2 signatures. The resonant modulations of the background signal are moderate for this spectrum, which affords the opportunity to measure both the temperature and species concentration from the spectral shape.

A Convex computer was used to least-squares fit the spectra acquired from the combustion of the nitramine strand using a computer program developed at Sandia, Livermore (Clark, 1986). The fitting process optimizes the combination of resonant species concentration and temperature that matches the experimental data. An example of the typically very good fits is shown in Fig. 5.

Figure 6 is a presentation of the results of fits to 24 individual spectra from a burn at 23 atm.. The temperature and concentration of the three resonant species are plotted as a function of distance above the burning propellant. The predicted equilibrium values (Gordon and McBride, 1976) are shown as thick, solid horizontal lines above the flame parameter they represent. The longer, thin solid lines are least-squares fits to the data points. The H_2 concentration results are divided by two for this presentation because their full-scale values confuse visualization of the N_2 data.

The first few laser shots reflect the ignition transient through the initial steep rise of the temperature and concentrations. During the transient, the flame merely spreads over the surface and the propellant does not regress. It is apparent that the propellant is already burning near its equilibrium parameters once the ignition transient is over, and the data are not indicative of any reaction zones close to the surface. After the ignition phase, the parameters remain reasonably constant until the flame starts to cool off after 7 mm above the surface. The cooling may be the result of helium diffusion into the flame. The agreement between the equilibrium values and experimental measurements is very good;

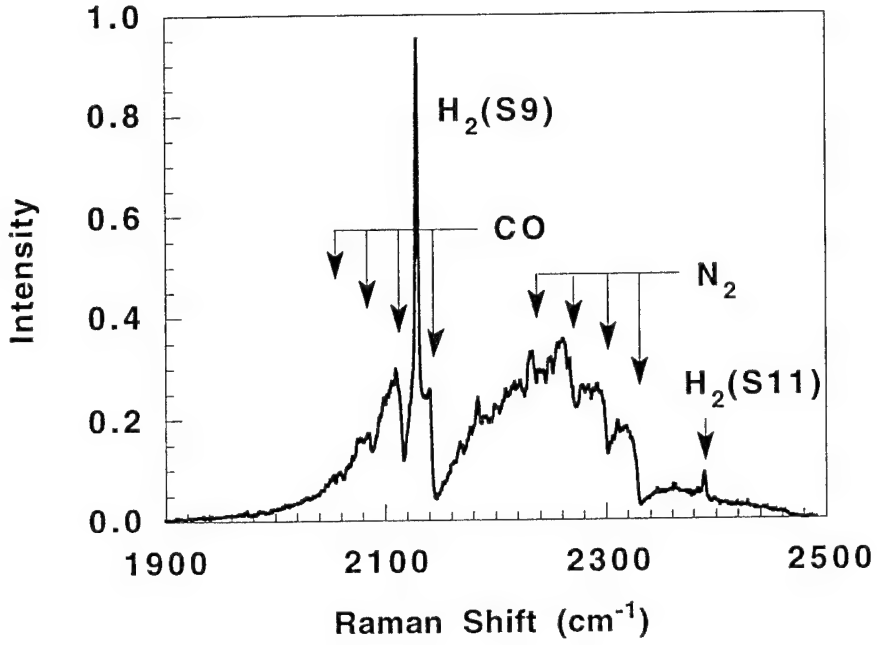


Figure 4. Single 10^{-8} sec pulse CARS spectrum from HMX/TMETN propellant at 23.1 atm of helium background pressure and 2.4 mm above propellant surface.

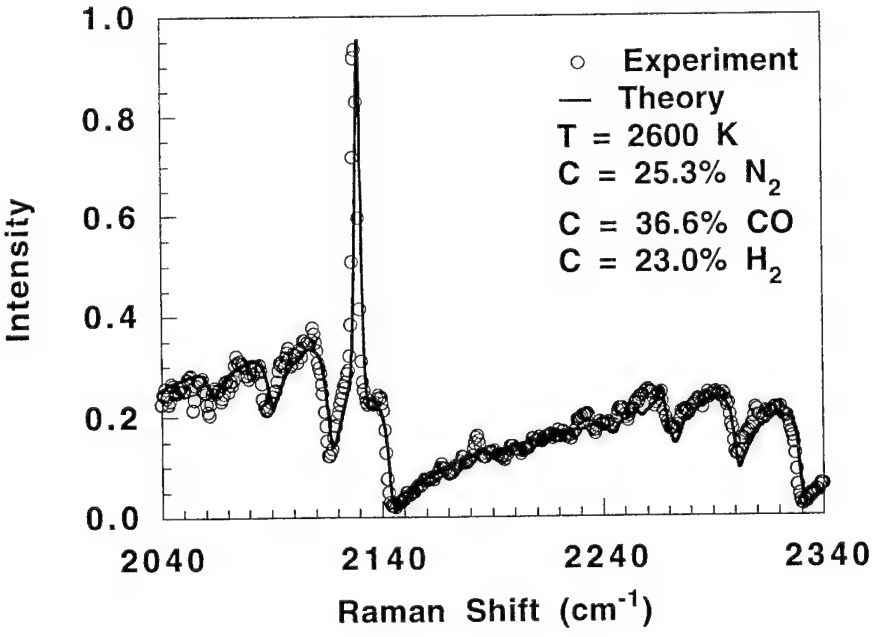


Figure 5. Comparison of theoretical and experimental CARS spectra. Experimental data are from Fig. 4.

the measurements are within 5% of the equilibrium prediction for CO and N_2, and temperature is within 2%.

The data of Fig. 6 indicate that this experiment has measured equilibrium product distributions and, while the data are useful for confirming this portion of the combustion, the more revealing chemical reactions near the propellant surface were not interrogated with this experiment .

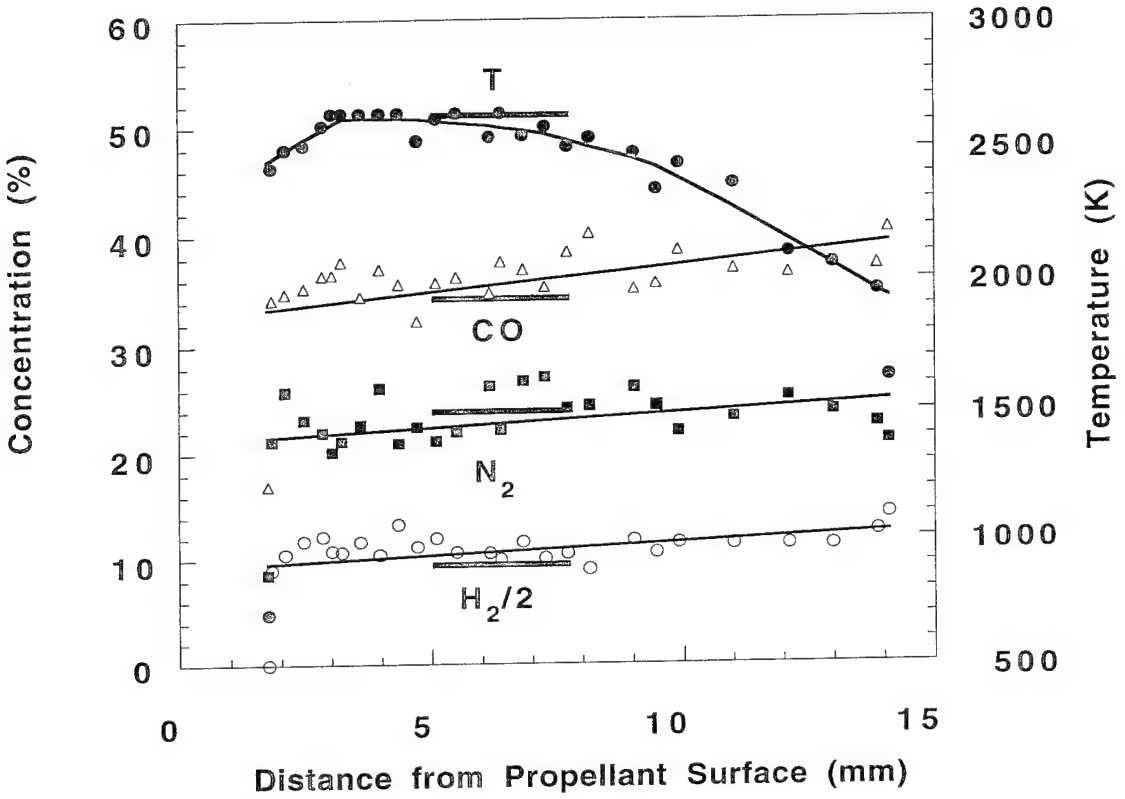


Figure 6. Summary of CARS measurements from HMX/TMETN combustion at 23.1 atm. The thick horizontal bars above each experimental parameter represent the value predicted from chemical equilibrium calculations. The thin lines are least-squares fits to the data points.

Near surface experiments. Experiments were performed in the laser, servo-controlled, motorized combustion vessel which permits spatial control of the all-important propellant surface region. This enables the acquisition of CARS spectra from the near-surface region of nitramine combustion at elevated pressure. Folded BOXCARS spectra provide point measurements of species and temperature. Examples of the acquisition of CARS spectra from the near-surface region of solid propellant combustion at elevated pressure are shown in Figs. 7 and 8.

Figure 7 was acquired at 9.8 atm using folded BOXCARS phase matching with a cylindrical resolution element of 100μ dia. × 3 mm long. It shows resonant modulations from HCN and CO at low temperature. This is expected from the propellant flame models that predict intermediate chemical species such as HCN and low temperature near the surface.

The propellant flame models (Hatch, 1987) predict a competition between two major reaction pathways in HMX combustion. One mechanism includes HCN, and the other H_2CO. The observation of H_2CO is an important step toward discerning reaction pathways in nitramine combustion, and Fig. 8 demonstrates this achievement. It is a single-shot spectrum from the near-

surface region of HMX burning at 12.8 atm. It shows signatures from H_2CO and CH_4. CH_4 has also been observed in pyrolysis experiments on HMX, but the binder chemistry may additionally be responsible for some portion of the resonant signatures. Computer analysis of the spectra in Figs. 7 and 8 was not attempted because the fitting algorithms did not contain the molecular parameters of HCN or H_2CO.

Line CARS. Enhanced spatial resolution techniques provide "line" CARS images of species profiles for temperature and gradient measurements. This capability has been applied to nitramine propellants to study possible different reaction pathways. The CARS image was formed by orthogonal cylindrical field lenses, 250 mm focal length in the horizontal plane and 600 mm in the vertical plane. This
resulted in a CARS line (focal image) of $150\mu \times 400\mu$. The collection optics map the CARS image onto the slit of a 0.6 m spectrograph. The slit image is 20 channels high on the detector, and results
in 20μ spatial resolution. Data from this experiment are presented in Fig. 9. The line CARS spectra
are dispersed in frequency along the horizontal axis, and vertical distance from the propellant surface

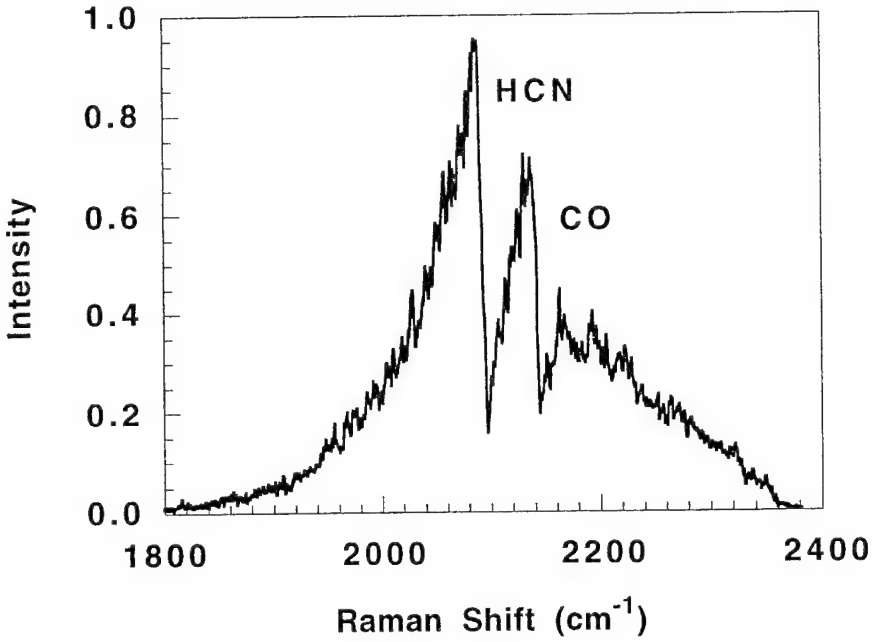


Figure 7. Single-shot CARS spectrum from solid propellant combustion in the servo-controlled burner. The pressure was 9.8 atm. These data were acquired approximately 100 microms from the surface.

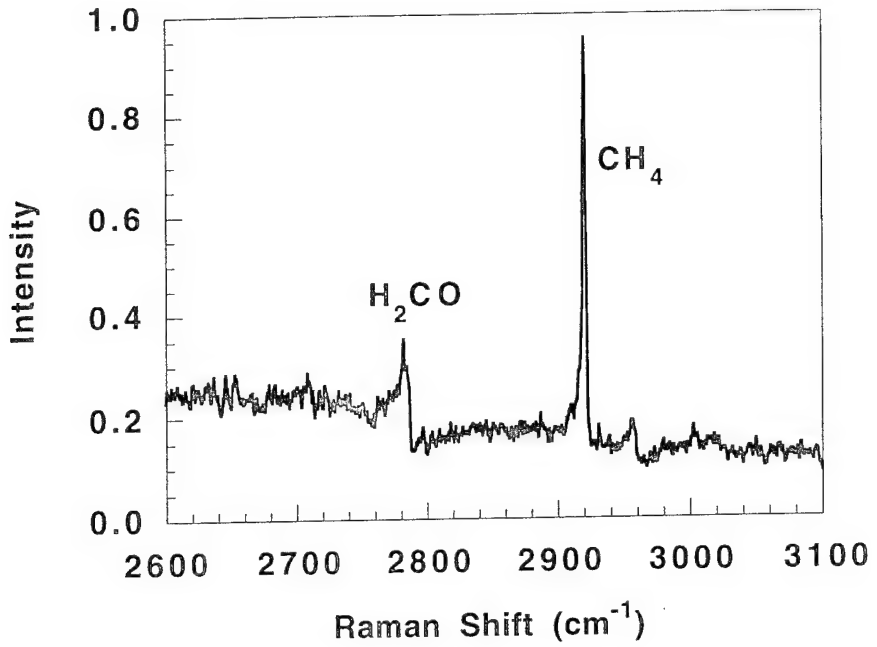


Figure 8. Single-shot CARS spectrum from solid propellant combustion in the servo-controlled burner. The pressure was 12.8 atm and the spectrum was acquired 100 microns from the surface.

is indicated in the perspective projection. The distance scale is arbitrary at this point, requiring further experiments to determine its range and resolution. Figure 9 was obtained from an RDX-based propellant at 16 atm. The spatial distributions of HCN and CO are different, HCN peaks closer to the surface where there is little CO. The spectra are quite complex and several features remain to be identified in the region around 1900 cm^{-1}.

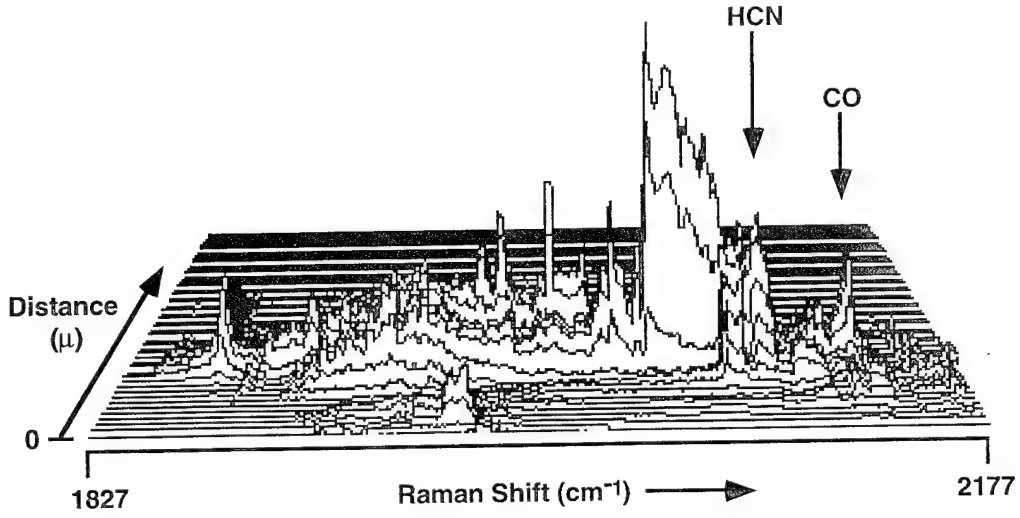


Figure 9. Single shot, linear CARS image from XM39 (LOVA) propellant combustion at 18 atm.

1-atmosphere data. An alternate experimental method to enhance spatial resolution is to burn the propellants at 1 atm which expands the reaction zone. The strands require preheating for combustion at 1 atm which is provided in our experiment by an internal heater described previously. An example of a CARS spectrum acquired from HMX burning at 1 atm is shown in the following figure.

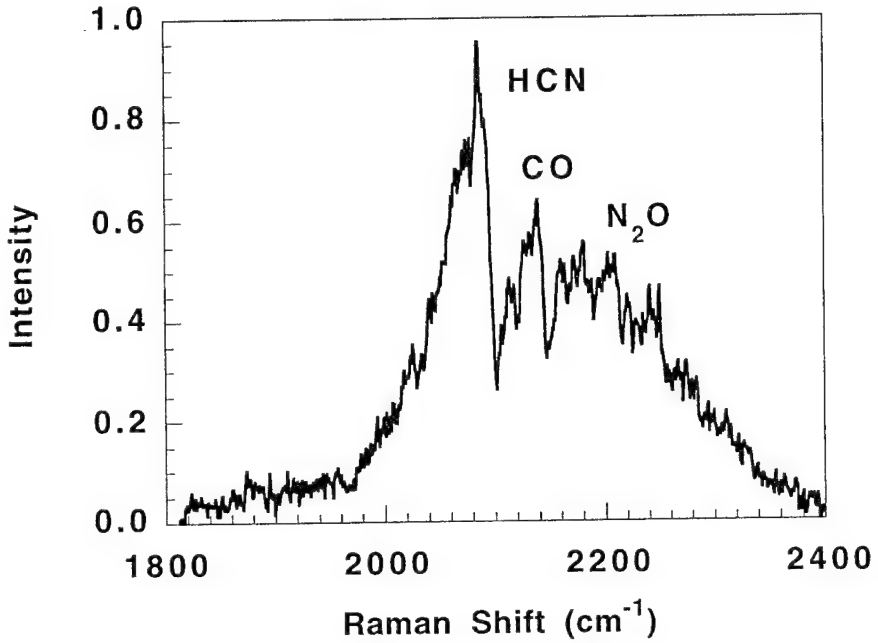


Figure 10. Single-shot CARS spectrum from solid propellant combustion at 1 atm. Spectrum was acquired approximately 100 microns from the surface.

In addition to the HCN and CO observed near the surface at elevated pressure (Fig. 7), the 1 atm combustion indicates N_2O is present near the surface. The N_2O modulations are noisy due to low concentration of this molecule.

DEGENERATE FOUR-WAVE MIXING

CARS is generally not sensitive to minor constituents unless it is electronically resonantly enhanced (Verdieck et al., 1984; Attal-Trétout et al., 1990). Electronic resonance CARS is not easy to implement particularly in regard to single pulse measurements. Major equilibrium species normally used for CARS thermometry such as N_2 or CO may not be present in large enough concentrations close to the surface of nitramines (see Fig. 10), so complementary thermometry techniques need to be investigated as well as ones that are sensitive to the expected intermediate combustion products, including radical constituents. Laser-induced fluorescence (LIF) has been used to measure minor species in propellant flames (Edwards et al., 1986; Parr and Hanson-Parr, 1987) but quantitative interpretation of the results is difficult due to quenching effects which are difficult to evaluate, particularly in transient environments and at high pressures. Furthermore, single-pulse LIF spectral quality is not nearly as good as that seen in single-pulse CARS

measurements in similar media. A recent application of a nonlinear optical technique, DFWM, may afford the opportunity to quantitatively measure these minor species with good S/N.

DFWM (Shen, 1984; Abrams et al., 1983) is a coherent process that does not suffer from the quenching effects of LIF that often inhibit quantitative measurements of minor species (Parr and Hanson-Parr, 1987). Dreier and Rakestraw (1989, 1990) have used DFWM to measure OH and NH rotational temperatures in a flame, and Ewart et al. (1989) implemented a 2-D configuration of the technique. More recently, it has been applied to high pressure combustion by Bervas et al. (1992) and Feikema, *et al.* (1992). The CH radical was detected and studied by Williams et al. (1992). A novel 2-D imaging application that relieves some alignment constraints was implemented by Winter and Radi (1992). This work is described later in this paper. In DFWM, all lasers including the pumps, probe and signal beam are at the same frequency, which is resonant with an electronic transition of the molecule. Phase matching is achieved in one approach via counter propagating pump beams referred to as the forward wave, $\vec{k}_f$, and the backward wave, $\vec{k}_b$ (Fig. 11).

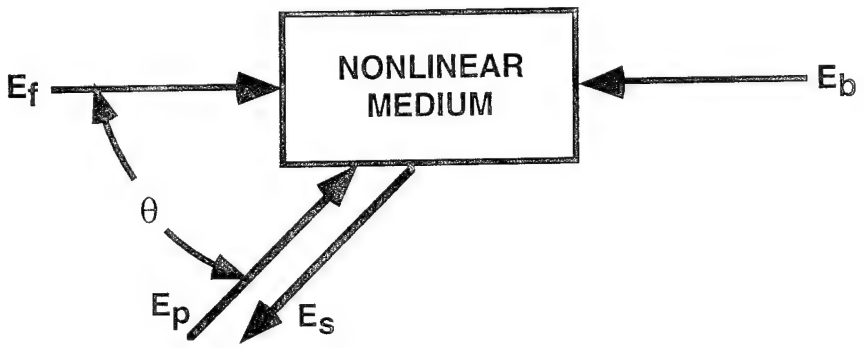


Figure 11. Pump and probe beam propagation geometry for generation of the DFWM signal beam.

$$\Delta\vec{k} = 0 = \vec{k}_{\text{signal}} + \vec{k}_{\text{f}} + \vec{k}_{\text{b}} + \vec{k}_{\text{probe}}$$

$$\text{with } \vec{k}_{\text{b}} = -\vec{k}_{\text{f}}$$

$$\vec{k}_{\text{signal}} = -\vec{k}_{\text{probe}}$$

Thus the signal beam propagates backward along the probe, as shown in Fig. 11, and can be separated by a beamsplitter. The interaction between the probe laser and each pump creates a phased array of dipole oscillators in the medium (Fig. 12) that acts as a grating to coherently scatter the other pump beam into the direction of the signal beam. The process is analogous to Bragg diffraction in crystals.

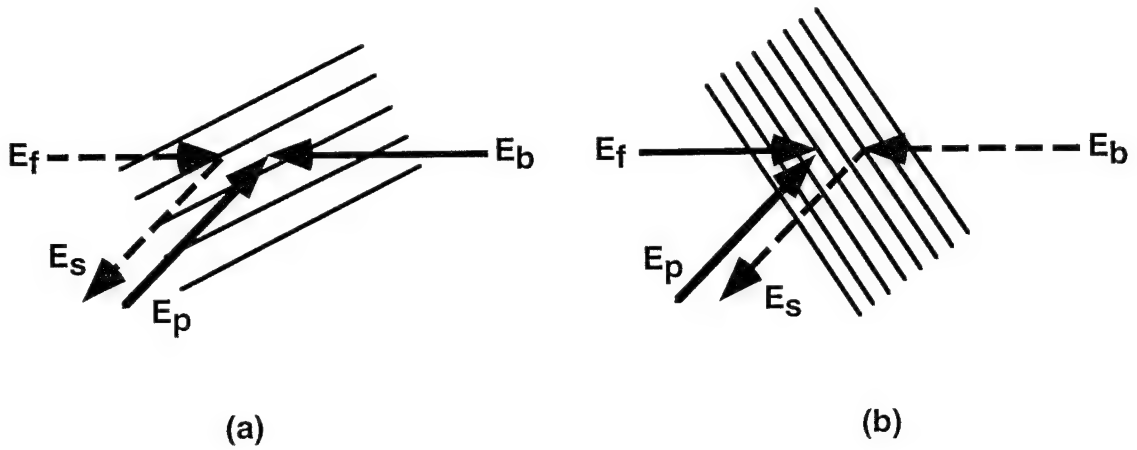


Figure 12. Grating representation of signal production in degenerate four-wave mixing

In some aspects, DFWM is a simpler nonlinear spectroscopy since the lasers are all at the same frequency, as opposed to CARS which requires at least two different input laser frequencies. In multi-species CARS approaches, three different frequencies are usually required (Eckbreth and Anderson, 1985). The simplification of DFWM produces some experimental difficulties, however; discrimination against the pump beams is necessary in the detection optics since all frequencies are degenerate. Non-degenerate techniques like CARS offer an advantage because optical filters can effectively discriminate against the pump laser photons.

Experimental Apparatus

The typical experimental geometry is shown in Fig. 13. The uv wavelengths required of the absorption transitions are provided in a Lumonics 500D dye laser that is pumped by the 2nd or 3rd harmonic of Nd:YAG. The OH transitions were accessed by frequency doubling a visible dye laser to produce narrowband (0.001 nm) pump and probe beams. The first beam splitter separates 30% of the uv laser to produce a probe beam that is directed through the flame. The forward pump

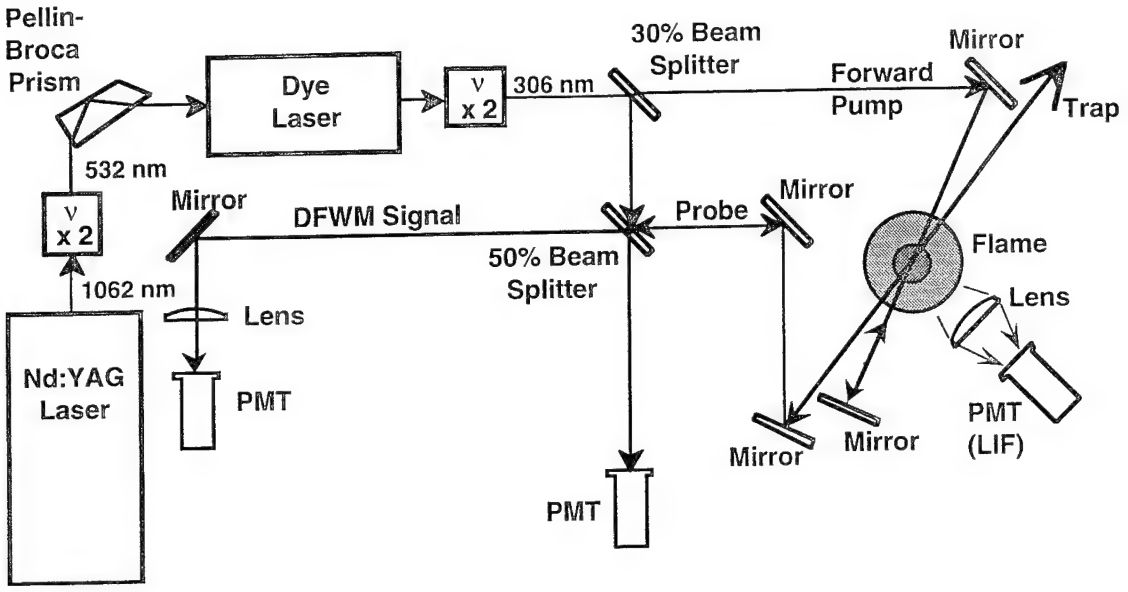


Figure 13. Optical layout for degenerate four-wave mixing. Laser wavelength is at the OH absorption bands.

crosses the probe, within the flame, and subsequently is retroreflected back along itself to form the backward wave. The signal beam propagates backward along the probe direction and is separated from the probe at the 50% beamsplitter. It is then detected on the photomultiplier, sampled by a gated integrator, and digitized and stored in a computer. Similarly, the LIF is detected at 90° from the direction of the pump beams. The dye laser intensity is sampled through the back of the 50% beamsplitter by a second photomultiplier. Scanning the frequency of the dye laser produces the DFWM and LIF spectrum.

DFWM Results and Discussion

High resolution scanned spectra. Shown in Fig. 14 are the simultaneously acquired LIF and DFWM spectra of OH in an atmospheric pressure, premixed, methane/air flame. These data were obtained by scanning the narrowband laser through the absorption transitions of OH. The portion of the spectrum containing the R_1 and R_2 branches of the $A^2\Pi(v'=0) \Leftarrow X^2\Sigma^+(v''=0)$ is shown. The spatial resolution was determined by the intersection of the pump and probe beams and was approximately 1 mm^3. The Doppler free DFWM spectrum has narrower linewidths than the LIF spectrum, thus higher resolution and comparable sensitivity to the LIF spectrum.

Dreier and Rakestraw, (1989, 1990) have shown that DFWM line intensities of OH transitions in atmospheric flames scale simply with the square of the rotational state number density, whereas LIF intensities are linearly proportional to the state population but have additional, complicated quenching corrections that must be applied for concentration measurements. The quenching corrections increase the relative error associated with LIF measurements. Quantitative DFWM measurements would complement CARS data of temperature and the major combustion species and provide more of an experimental database to compare with predictions from combustion models.

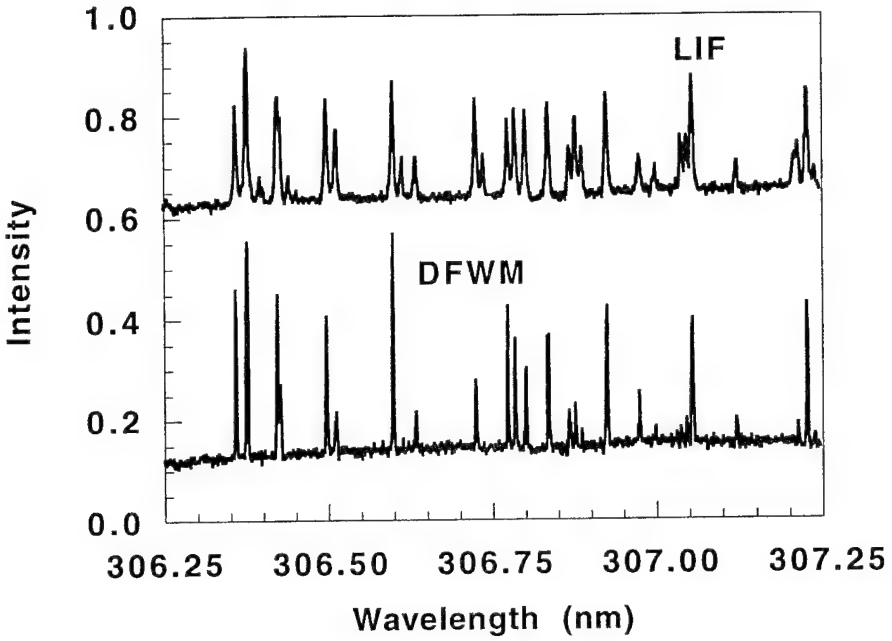
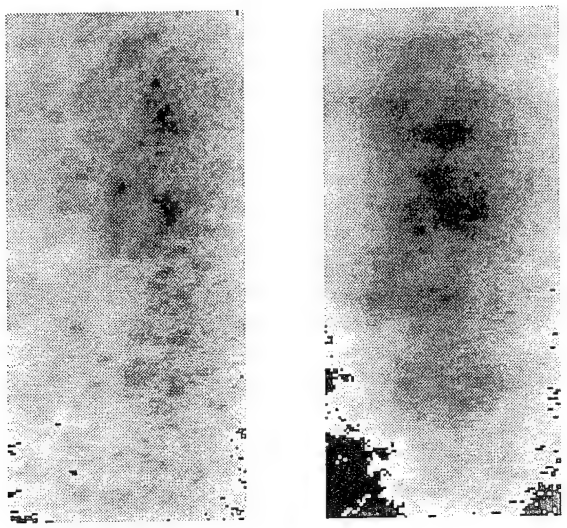


Figure 14. Simultaneously acquired LIF and DFWM spectra from a methane/air flame at 1 atm.

2-D imaging with double-phase conjugate four-wave mixing. A novel configuration has been developed by Winter and Radi (1992) for performing degenerate four-wave mixing experiments using optical phase conjugation from stimulated Brillouin scattering (SBS) in a cell. It can be difficult to maintain alignment and overlap between the two counter-propagating pump beams in the typical DFWM geometry (Fig. 13), particularly in combustion systems which present thermal and density gradients. The gradients produce distortions in the phase and direction of the pump beams. DFWM has been demonstrated for OH in a flame using counter-propagating pump beams that are phase conjugate. The phase conjugation generates a backward-going wave which still possesses the anomalies and distortions and will identically follow the path of the incident beam. When this backward-going wave passes through the distorting medium a second time (only now in the reverse direction), the original distortions are completely removed. This approach greatly simplifies DFWM experiments by relaxing alignment constraints and sensitivities to index of refraction gradients in the flow.

Optical phase conjugation is achieved by focusing the first pump beam into a quartz cell containing hexane instead of reflecting it back on itself with a mirror. The liquid in the cell produces a backwards-propagating beam via SBS. Because SBS introduces a slightly different frequency in the scattered pump beam, we refer to the interaction process as nearly-Degenerate Four-Wave Mixing in accordance with the literature (Abrams et al., 1983). Winter and Radi analyzed the relative intensities and the line shapes of the rotational transitions in the $A^2\Pi(v'=0) \Leftarrow X^2\Sigma^+(v''=0)$ system of OH. The nearly-DFWM technique was compared with DFWM, using a conventional set up in which a mirror reflects the pump beam back on itself. The nearly-DFWM method is essentially as sensitive as DFWM, and the technique allows temperature and concentration measurements in hostile combustion systems by relaxing alignment constraints and sensitivities to the index of refraction gradients in the flow. More recently, this approach has been applied for imaging of the OH distributions in a flame. Data were taken using DFWM with and without generation of the backward-going pump beam using SBS. These were recorded from laminar and

turbulent non-premixed methane jet flames. The nozzle diameter was 2.5 mm and the data were taken ~17.5 diameters downstream. The images shown in Fig. 15 are ~2 diameters in spatial extent. Comparing conventional DFWM to the SBS DFWM shows significantly better signal-to-noise using the double-phase-conjugate geometry. The data from the conventional DFWM fluctuate to a much greater degree. Often, no signal can be recorded, presumably due to misalignment of the sheets after passing through thermal gradients in the flow. In contrast, the double-phase-conjugate geometry provides reliable and consistent data even in the presence of the turbulent flame.



(a) (b)

Figure 15. Images of OH intensities of a turbulent premixed methane/air flame produced by conventional DFWM (a) and double phase-conjugate four-wave mixing (b).

FUTURE WORK

Experiments are planned to measure fundamental parameters such as the Raman cross section of HCN so computer models can predict temperature and species from the CARS signature of this molecule. Procedures need to be developed and tested for normalization of "line" CARS spectra. The raw images require normalization of the pump beam intensities, including information on the spatial distribution of intensity in the focal region. This information is contained, for example, in a spectral image from a nonresonant gas sample that can be acquired separately and then divided into the flame image. Dividing one 2-D image by another can introduce inaccuracies, especially in the wings of the spatial distribution where the intensity of both fields is falling rapidly. The propellant surface can easily be within the region of intensity gradients, yet this is precisely where the most accurate measurements are required, and thus the need for careful normalization. High pressure pre-mixed flames provide a stable, fixed reaction zone and uniform post flame zone that can be used to test normalization techniques.

The feasibility of broadband approaches to DFWM needs to be addressed so that simpler approaches to single-pulse thermometry and species concentration measurements can be examined for combustion experiments. Important molecules to measure include CN, CH, and NO radicals

because they influence the nitrogen chemistry. Issues that need to be investigated include frequency doubling a broadband laser, or Raman shifting techniques to produce a broadband uv source. Our current efforts involve generation of a broadband uv source by pumping a dye laser with a suitable harmonic of Nd:YAG or an ArF excimer laser to provide broadband sensitivity for the CN radical at 388 nm. Concentration measurements will rely on knowledge of the absolute intensity of the scattered radiation. Calibration techniques need to be addressed for DFWM, since there is no signal from χ^{nr} for in situ referencing (Eckbreth, 1988), as in CARS.

SUMMARY

CARS and DFWM are coherent nonlinear, laser-based, optical diagnostics with high spatial and temporal resolution that accommodate well to the high interference and restricted optical access environments typical of solid propellant combustion experiments. The challenge of propellant combustion has required techniques that extend the spatial resolution of these modern diagnostic approaches. A sophisticated strand-burning facility was developed and employed to provide control of the propellants during combustion. CARS measurements confirmed the equilibrium chemistry (temperature and species concentration) of nitramine propellant formulations burning at elevated pressures. CARS signatures from two competing chemical pathways (HCN and H_2CO) were observed in the near-surface region of nitramine combustion. A 1-D imaging configuration, realized with cylindrical optics and a 2-D detector, provided enhanced spatial resolution of 20μ and single-shot data on species and temperature adjacent to the strand surface. The "line" CARS data demonstrated viable signal strength and spatial resolution, but further analysis of normalization techniques is required to produce quantitative results of temperature and concentration gradients. An experimental program is currently underway to apply DFWM in the near-surface region where traditional CARS approaches may fail because normal major molecular species are absent. DFWM has the potential to measure the minority concentrations and temperature of important radical and intermediate species.

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COMMENTS

W. Meier, DLR, Stuttgart, Germany. 1. What is the spatial resolution in length for the 1D CARS setup? Are the temperature and concentration profiles flat in that direction? 2. What is the computing time for a full least squares fit of a typical CARS spectrum? How many parameters are fitted?

Authors' Reply. The axial resolution was 3 mm; the propellant cross section was 6 mm × 6 mm. As the propellant regresses with a flat surface, the flame is one dimensional with variation perpendicular to the surface. There is no variation of the combustion environment in the direction of the axial resolution element as long as the axial resolution is smaller than the propellant dimensions.

The average CPU time for the least squares fits of the CARS spectra was 3 hours on a Convex computer; modern computers may be 10 times faster. The computer time required to derive quantitative temperature and concentration measurements depends on several factors: the speed of the computer, the spectral range of the data, the number of resonant species (# of transitions), the numerical method of convolution used to model the CARS spectrum (e.g., partial coherence), and the algorithm used for data extraction, i.e., least squares fits, library interpolation, or quick fitter routines. The choices used for our data all maximize the time required because it was felt this would result in the most complete and accurate set of measurements. For more limited information, i.e., temperature from a N_2 spectrum at 1 atm, quick fitter routines can extract data at the 10 or 20 Hz rate of the laser, resulting in essentially real time data analysis. (J. H. Stufflebeam and A. C. Eckbreth)

H. F. R. Schöyer, ESA/ESTEC, The Netherlands. Comment If CARS or other diagnostic techniques are used to determine the composition of the combustion products in the flame zone (spatial resolution), the pressure may be reduced to increase the flame zone, and, hence, increase spatial resolution.

Changing combustion pressure may change the reaction mechanism. To verify whether or not that is the case, one may use the measured propellant-burn rate vs. pressure. The relation is usually given in a DeVille law: $r=a \cdot p^n$ (r burning rate, P pressure, a burn rate coefficient, n burn rate exponent). It may be shown that n=1/2 the order of the overall reaction. If n therefore changes between low and high pressure, one knows that the reaction mechanism (combustion) has changed; therefore, lowering the pressure will not yield information which is valid (or could be translated/interpreted) for high pressure combustion. (By the way, this was an excellent paper!)

Authors' reply. The comment is well taken. CARS is one of the few diagnostic techniques capable of working in such an extended pressure range and thus could be used to investigate the changes in the chemical reaction mechanism responsible for the burn rate anomaly. (J. H. Stufflebeam and
A. C. Eckbreth)

K. Kohse-Höinghaus, University of Bielefeld, Germany. Please comment on the need for DFWM thermometry vs. CARS thermometry and which temperature indicator will you most probably be using?

Authors' reply. Near the propellant surface there is predicted to be (and experimentally confirmed) small concentrations of molecules traditionally used for CARS thermometry. There is also the desire to measure the concentrations of minority species that are near the surface. DFWM offers a solution to both these objectives. Near the surface, DFWM may be used for thermometry and concentration measurements, while CARS is used throughout to measure the more abundant constituents.
(J. H. Stufflebeam and A. C. Eckbreth)

H. J. J. ter Meulen, University of Nÿmegen, The Netherlands. Could you comment on the possibility of determining temperatures and species concentrations by DFWM?

Authors' reply. The DFWM signal is proportional to $\Delta N^2 \mu_{12}^4$ for saturated transitions. Here ΔN is the population difference between probed levels, and μ_{12} is the transition dipole moment. A broadband DFWM spectrum that includes several transitions of a molecule could be used to determine temperature from the relative population of the rotational levels. This technique has been demonstrated at Stanford [Yip, B., Danehy, P. M., and Hanson, R. K., 1992. Degenerate 4-Wave-Mixing Temperature-Measurements in a Flame, *Optics Letters,* Vol. **17**, pp. 751-753]. Broadband approaches are important because they enable high temporal-resolution measurements with pulsed lasers. Calibration of species concentration can be obtained from simultaneous absorption experiments or from comparison with spectra from a calibrated gas mixture. (J. H. Stufflebeam and A. C. Eckbreth)